

An ab initio quantum chemical investigation of the structure and stability of ozone-water complexes



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ABSTRACT

Ab initio quantum chemical calculations have been carried out to investigate the structure and stability of 1:1 and 1:2 ozone-water complexes. All the geometries have been optimized at the CCSD level of theory using aug-cc-pVDZ and aug-cc-pVTZ basis sets. The importance of correlation-consistent basis sets in deciding the nature of critical points on these complexes is emphasized. An analysis based on the dipole moment of the complexes and the charge distribution on atoms follows. The effect of ozone molecule on the structure and properties of water dimer is also investigated. Values of the vertical electronic excitation energy and the corresponding transition dipole moment have been calculated for the ozone-water complexes using the multi-reference-configuration-interaction method and the aug-cc-pVTZ basis set. The calculated shift in vibrational frequencies due to complex formation is compared with the earlier reported experimental and theoretical values.

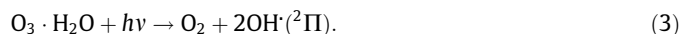
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1. Introduction

Ozone plays an important role in the chemistry of the upper atmosphere. Therefore, its molecular structure and electronic states have been studied extensively over the years [1,2]. The chemistry of ozone in the ozone layer involves several other species in the atmosphere [3,4]. Therefore, it is very important to know the nature of the interaction of ozone with other molecules. In the present study the ozone-water complex has been chosen for a detailed investigation as it is one of the key complexes in the atmosphere. The O(¹D) atom generated during UV photolysis of ozone reacts with H₂O to produce hydroxyl radicals (OH[•]):



The hydroxyl radical is one of the most important oxidants in the atmosphere and it plays an important role in the depletion of the ozone layer [5]. The ozone-water complex, O₃-H₂O, was proposed as a possible source of the hydroxyl radical in the troposphere. Frost and Vaida [6] estimated that 0.001–0.01 % of tropospheric ozone exists as ozone-water complex. The hydroxyl radical might be produced efficiently through the photolysis of the O₃-H₂O complex [7–9]:



In this context the knowledge of the geometry and the electronic spectrum of the O₃-H₂O complex becomes very important. Hydration could shift the absorption peak of O₃ significantly and affect the formation of free radicals.

A few ab initio calculations had already been carried out for the O₃-H₂O complex [10–17]. From MP2/6-31G(d,p) and MP4SDTQ(d,p) calculations, it was found that the terminal oxygen atom of ozone was tilted towards one of the hydrogen atoms of the water molecule [10]. From MP2SDQ(4-31G) calculations, Zhakhrov et al. [11] found that one of the hydrogen atoms of H₂O orients towards one of the terminal oxygen atoms of the ozone molecule. Recently, Tachikawa and Abe [12,13] have carried out ab initio calculations at the QCISD(T)/6-311++G** and CCSD/6-311++G** levels of theory. It was found that at the QCISD(T)/6-311++G** level, there are three important possible structures for the ozone-water complex: dipole, cis and trans. In the dipole structure the central oxygen atom of the ozone molecule and all the three atoms of the water molecule are in the same molecular plane, thus belonging to the point group C_s. The cis and the trans geometries were found to be planar, with the terminal oxygen atom of ozone making a hydrogen bond with the water molecule. At the CCSD/6-311++G** level of theory, a new geometry called eclipse was found to be the most stable.

More recently, Laboda and Goncharuk [14] have carried out a systematic study of the interaction between water clusters and ozone molecule using MP2/MP4 methods and the 6-311++G** basis set. They have considered up to six water molecules with one ozone molecule. In their studies, they have found two stable

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complexes for O_3-H_2O , namely “eclipse” and “side” (see below). The interaction energy between ozone and water clusters in the $O_3-(H_2O)_2$ complex was found to be the largest among all the $O_3-(H_2O)_n$ ($n = 1-5$) complexes. Only the $O_3-(H_2O)_6$ complex was found to have more interaction energy between ozone and the water cluster when compared to the $O_3-(H_2O)_2$ complex.

Some experimental studies have also been reported in the literature for the O_3-H_2O complex [10,16,18]. Tachikawa and Abe [12] had assigned the dipole structure to the microwave spectrum of the ozone-water complex. Later, Tsuge et al. [16] studied the ozone-water complex in a neon matrix and concluded on the basis of their calculations that the eclipse geometry was the most stable. Thus the structure of ozone-water complex continues to be a matter of interest.

The electronic spectrum of the ozone-water complex is also a matter of controversy in the literature. Tachikawa and Abe [13,15] reported a new charge transfer band in the ozone-water complex using time-dependent density functional theory, but later when they carried out calculations at the SAC-CI level, they did not find any charge transfer band. The SAC-CI calculations were done only for the eclipsed geometry. In this geometry the information about the $2^1A_1-1^1A_1$ transition was not given. The SAC-CI theory is a single reference method. Therefore, it may not be reliable for studying transitions to the excited states of same symmetry. Given the multi-reference character of the ozone molecule, it may give the right trend in the excitation energy values but may not yield quantitative results.

We have carried out good quality ab initio calculations to locate and characterize these complexes, their relative stability, and to calculate the vibrational frequencies and the vertical electronic excitation energy values. By comparing the changes in the vibrational frequencies and the vertical excitation energy due to complex formation, we hope to provide information that can be useful in their experimental characterization.

2. Computational method

It is known that the ground state of ozone has a multi-reference character. As a result, not all computational methods work well for ozone [19]. The T1 diagnostic value for ozone is 0.03 and for ozone-water complex, it is 0.024. Therefore, the coupled cluster methods can be used for geometry optimization. The O_3-H_2O complex involves weak hydrogen bonds, and it is known that coupled cluster methods are suited for describing hydrogen bonds. It is also known that the coupled cluster methods describe the electronic properties of ozone better than other single determinant methods [20,21]. The dipole moment of ozone at the CCSD/aug-cc-pVTZ level of theory is found to be 0.63 D, which is close to the experimental value of 0.53 D [22,23]. We have used the CCSD method with 6-311G**+, aug-cc-pVDZ and aug-cc-pVTZ basis sets for optimizing the geometry of different ozone-water complexes. Single point energy calculations have also been carried out using the CCSD (T) method in conjunction with the aug-cc-pVTZ and aug-cc-pVQZ basis sets to improve the energetics. The interaction energy for the complex, relative to the isolated ozone and water molecules was computed using the supermolecule approach:

$$E_{int} = E_{complex} - [E_{ozone} + E_{water(monomer/dimer)}]. \quad (4)$$

The interaction energy was corrected for basis set superposition error (BSSE) using the counterpoise correction method proposed by Boys and Bernardi [24]. Interaction energies at the complete basis set limit (CBS) were obtained by extrapolating SCF (Hartree-Fock) and correlation energies separately. The extrapolation of the SCF energy was carried out using the two point extrapolation formula (using the TZ and QZ basis sets for the 1:1 complex and the DZ

and TZ basis sets for the 1:2 complex), known as a new style extrapolation: [25,26]

$$E_X = E_\infty - \frac{A}{X^5}, \quad (5)$$

where X is the cardinality (2 for DZ, 3 for TZ and 4 for QZ) of the basis set. The correlation energy value was extrapolated by a two point extrapolation method suggested by Huh and Lee [27]:

$$E_X = E_\infty - \frac{A}{(X + 0.50)^3} \quad (X = 2, 3), \quad (6)$$

$$E_X = E_\infty - \frac{B}{(X - 0.25)^3} \quad (X = 3, 4). \quad (7)$$

Here E_∞ refers to the extrapolated energy in both Eqs. (6) and (7). The multi-reference-configuration-interaction (MRCI) method is used to get the information on vertical excitation energy and transition dipole moment of different low lying singlet states of the complexes. All the calculations except the MRCI were carried out using the Gaussian-09 suite of programmes [28]. The MRCI calculations were done using the MOLPRO suite of programmes [29].

2.1. Results and discussion

As illustrated in Fig. 1 there are at least six possible stationary points for the 1:1 complex formed between ozone and water molecules and they are labeled cis, trans, dipole, side, leg and eclipse. Out of these six, the leg, the dipole and the eclipse geometries are non-planar, while the other three are planar. It can be seen from Table 1 that for different basis sets, the character of some of these stationary points changes from “transition state” (characterized by an imaginary frequency) to a true minimum. When the 6-311++C** basis set is used, only the eclipse and the side geometries are found to be true minima. When the aug-cc-pVDZ basis set is used, the eclipse and the dipole geometries are found to be transition states, while the other geometries are found to be true minima. This table also emphasizes the importance of correlation-consistent basis sets in studying such complexes. The origin of the imaginary frequencies can be understood as follows. There are two types of interaction present in the 1:1 complex. The first type is the interaction between the central oxygen atom of ozone and the water molecule. The second type involves hydrogen bonding between the water molecule and the terminal oxygen atom of ozone. The 6-311++C** basis set is a triple-zeta basis set that describes the first type of interaction better than hydrogen bonding. The aug-cc-pVDZ basis set is correlation-consistent. Therefore, it can describe hydrogen bonding as well as the oxygen–oxygen interaction. The aug-cc-pVDZ basis set tends to prefer conformers that involve hydrogen bonding (cis, trans, side and leg). Therefore, no imaginary frequency is obtained for these complexes. The 6-311++C** basis set prefers the conformer involving oxygen–oxygen interaction. Therefore, the eclipse geometry does not have any imaginary frequency.

To resolve the issue of the true minima, geometry optimization and frequency calculations were carried out using the aug-cc-pVTZ basis set, which is correlation-consistent as well as triple-zeta in nature. Only the dipole geometry was found to be a transition state and all other geometries were found to be true minima. The observed and calculated frequencies of the O_3-H_2O complex are listed in Tables 2 and 3, along with the frequency shifts resulting from the complex formation. In the eclipse, leg and dipole geometries, all the vibrational frequencies of ozone are found to be blue shifted ($\Delta\nu > 0$). In the cis, trans and side complexes, the symmetric and bending frequencies are blue shifted, but the antisymmetric frequency is red shifted. The calculated frequency shifts for the

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